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Die folgenden Angaben sind den vom Anmelder eingereichten Unterlagen entnommen

(54) Anorganische Pigmente enthaltende Pigmentpräparationen

(57) Die Erfindung betrifft Pigmentpräparationen, enthaltend
a) feste Verbindungen aus der Gruppe der Oxide von Titan, Zink, Zinn, Wolfram, Molybdän, Nickel, Wismut, Cer, Indium, Hafnium, Eisen und/oder Siliciumcarbid, Zinksulfid, Bariumtitanat, Calciumtitanat und/oder Silicium und/oder feste Siliciumverbindungen, in denen Silicium im stöchiometrischen Überschuß vorliegt, mit einem mittleren Durchmesser der Primärteilchen von < 500 nm, und
b) wenigstens ein Farbmittel, das sich von der unter a) genannten festen Verbindungen unterscheidet,
die sich durch eine gute Lichtechtheit der damit gefärbten Substrate auszeichnen.

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nin-, Chinacridon-, Dioxazin-, Isoindolinon-, Naphthalintetracarbonsäure- und Perylen- und Perylentetracarbonsäurereihe, ferner solche aus der Perinon-, Indigoid-,- Thioindigoid- und Diketopyrrolopyrrol-Reihe, sowie Metallkomplex-Pigmente von Azo-, Azomethin- oder Methinfarbstoffen oder verlackte Farbstoffe wie Ca-, Mg-, Al-Lacke von sulfonsäure- und/oder carbonsäuregruppenhaltigen Farbstoffen.

Als in Wasser lösliche organische Farbstoffe sind z. B. saure und basische Farbstoffe zu nennen und als in Wasser unlösliche Farbstoffe beispielsweise Dispersionsfarbstoffe oder Weißtöner (optische Aufheller). Als Beispiele für Dispersionsfarbstoffe seien genannt solche aus der Azo-, Disazo-, Anthrachinon-, Cumarin-, Isoindolenin-, Chinolin- und Methinreihe.

In einer bevorzugten Ausführungsform enthält die erfindungsgemäße Präparation als Farbmittel Oxide und/oder Nitride von Metallen, die im roten Spektralbereich von 600 nm $< \lambda <$ 700 nm stärker absorbieren als im blau-grünen Spektralbereich von 400 nm $< \lambda <$ 550 nm. Als solche Zusätze sind Pigmente aus Titannitrid mit einem mittleren Durchmesser von 1 nm bis 400 nm, bevorzugt 10 nm bis 120 nm oder dessen Agglomerate bevorzugt. Deren Herstellung kann z. B. gemäß US-A 5 472 477 erfolgen. Ebenfalls bevorzugte Farbmittel sind Ultramarine Pigmente, z. B. erhältlich bei der Firma Nubiola S.A., unter der Bezeichnung Nubix® Pigmente. Weiterhin bevorzugt ist Eisen(III)hexacyanoferrat(II).

Die Partikelgröße der übrigen Vertreter der Komponente a) liegt vorzugsweise bei 1 nm bis 500 nm, besonders bevorzugt 1 nm bis 120 nm. Auch diese sind u. a. nach dem in US-A 5 472 477 beschriebenen Verfahren erhältlich.

Dispergiermittel

Als Dispergiermittel werden Moleküle mit einer Molmasse von 1000 bis 500 000, bevorzugt 1000 bis 100 000 und insbesondere 1000 bis 10 000 g/mol angesehen. Die Dispergiermittel können nichtionische, anionische, kationische oder amphotere Verbindungen sein.

Als nichtionische Dispergiermittel sind beispielsweise zu nennen: Alkoxylate, Alkylolamide, Ester, Aminoxide und Alkylpolyglykoside.

Als nichtionische Dispergiermittel kommen weiterhin in Frage: Umsetzungsprodukte von Alkylenoxiden mit alkylierbaren Verbindungen, wie z. B. Fettalkoholen, Fettaminen, Fettsäuren, Phenolen, Alkylphenolen, Arylalkylphenolen, wie Styrol-Phenol-Kondensate, Carbonsäureamiden und Harzsäuren. Hierbei handelt es sich z. B. um Ethylenoxidaddukte aus der Klasse der Umsetzungsprodukte von Ethylenoxid mit:

a) gesättigten und/oder ungesättigten Fettalkoholen mit 6 bis 20 C-Atomen oder
b) Alkylphenolen mit 4 bis 12 C-Atomen im Alkylrest oder
c) gesättigten und/oder ungesättigten Fettaminen mit 14 bis 20 C-Atomen oder
d) gesättigten und/oder ungesättigten Fettsäuren mit 14 bis 20 C-Atomen oder
e) hydrierten und/oder unhydrierten Harzsäuren.

Als Ethylenoxid-Addukte kommen insbesondere die unter a) bis e) genannten alkylierbaren Verbindungen mit 5 bis 120, vorzugsweise 5 bis 60, insbesondere 5 bis 30 Mol Ethylenoxid in Frage.

Besonders bevorzugt sind nichtionische polymere Dispergiermittel.

Als polymere Dispergiermitteln sind beispielsweise die Verbindungen, die im Verzeichnis "Water-Soluble Synthetic Polymers: Properties and Behavior" (Volume I + II by Philip Molyneux, CRC Press, Florida 1983/84) genannt sind, anzusehen.

Weitere polymere Dispergiermittel sind beispielsweise wasserlösliche sowie wasseremulgierbare Verbindungen in Frage, z. B. Homo- und- Copolymerisate, Pfropf- und Pfropfcopolymerisate sowie statistische Blockcopolymerisate.

Besonders bevorzugte polymere Dispergiermittel sind beispielsweise AB-, BAB- und ABC-Blockcopolymere. In den AB- oder BAB-Blockcopolymeren ist das A-Segment ein hydrophobes Homopolmyer oder Copolymer, das eine Verbindung zum Pigment sicherstellt und der B-Block ein hydrophiles Homopolymer oder Copolymer oder ein Salz davon und stellt das Dispergieren des Pigmentes im wäßrigen Medium sicher. Derartige polymere Dispergiermittel und deren Synthese sind beispielsweise aus EP-A-518225 sowie EP-A-556 649 bekannt.

Weitere Beispiele geeigneter polymerer Dispergiermittel sind Polyethylenoxide, Polypropylenoxide, Polyoxymethylene, Polytnmethylenoxide, Polyvinylmethylether, Polyethylenimine, Polyacrylsäuren, Polyarylamide, Polymethacrylsäuren, Polymethacrylamide, Poly-N,N-dimethyl-acrylamid, Poly-N-isopropylacrylamide, Poly-N-acrylglycinamide, Poly-N-methacrylglycinamide, Polyvinylalkohole, Polyvinylacetate, Copolymere aus Polyvinylalkoholen und Polyvinylacetaten, Polyvinylpyrrolidon, Polyvinyloxazolidone, Polyvinylmethyloxazolidone.

Weiterhin sind natürliche polymere Dispergiermittel wie Cellulose, Stärke, Gelatine oder deren Derivate als polymere Dispergiermittel von Bedeutung. Besonders kommen Polymere aus Aminosäureeinheiten z. B. Polylysin, Polyasparaginsaure usw. in Frage.

Als anionische Dispergiermittel sind beispielsweise zu nennen: Alkylsulfate, Ethersulfate, Ethercarboxylate, Phosphatester, Sulfosucinate, Sulfosuccinatamide, Paraffinsulfonate, Olefinsulfonate, Sarcosinate, Isothionate, Taurate und Lignin ische Verbindungen.

Besonders bevorzugt sind anionische, polymere Dispergiermittel.

Geeignete anionische polymere Dispergiermittel sind insbesondere Kondensationsprodukte von aromatischen Sulfonsäuren mit Formaldehyd, wie Kondensationsprodukte aus Formaldehyd und Alkylnaphthalinsulfonsäuren oder aus Formaldehyd, Naphthalinsulfonsäuren und/oder Benzolsulfonsäuren, Kondensationsprodukte aus gegebenenfalls substituiertem Phenol mit Formaldehyd und Natriumbisulfit.

Weiterhin kommen in Frage Kondensationsprodukte, die durch Umsetzung von Naphtholen mit Alkanolen, Anlagerung von Alkylenoxid und mindestens teilweiser Überführung der terminalen Hydroxygruppen in Sulfogruppen oder Halbester der Maleinsäure, Phthalsäure oder Bernsteinsäure erhältlich sind.

Geeignet sind außerdem Dispergiermittel aus der Gruppe der Sulfobernsteinsäureester sowie Alkylbenzolsulfonate.

Polyvinylalkohol, Poly[redacted]pyrrolidon, Methylcellulose u. a. dem Fachmann [redacted]nte Mittel, soweit sie die Stabilität der Drucktinte, das Druckverhalten und das Trocknungsverhalten auf Papier nicht negativ beeinflussen.

Als weiterer Zusatz sind Verbindungen aus der Gruppe der Terpene, Terpenoide, Fettsäuren und Fettsäureester zu nennen. Als bevorzugte Verbindungen seien dabei genannt:
Ocimen, Myrcen, Geraniol, Nerol, Linalool, Citronellol, Geranial, Citronellal, Neral, Limonen, Menthol, beispielsweise (–)-Menthol, Menthol oder bicyclische Monoterpene, gesättigte und ungesättigte Fettsäuren mit 6 bis 22-C-Atomen; wie beispielsweise Stearinsäure, Ölsäure, Linolsäure und Linolensäure oder Mischungen davon.

Grundsätzlich können die Pigmentpräparationen noch Konservierungsmittel, weitere Tenside und gegebenenfalls auch pH-Regler enthalten.

Beispiele für pH-Regler sind NaOH, Ammoniak oder Aminomethylpropanol, N,N-Dimethylaminoethanol.

Beispiele für Konservierungsmittel sind Methyl- und Chlormethyl-isothiazolin-3-on, Benzisothiazolin-3-on oder Mischungen davon.

Die erfindungsgemäßen Pigmentpräparationen enthalten vorzugsweise:

0,05 bis 20 Gew.-%, vorzugsweise 0,1 bis 10 Gew.-%, der Komponente a) bezogen auf das Farbmittel der Komponente b),
1 bis 99,95 Gew.-%, vorzugsweise 1 bis 65 Gew.-% eines Farbmittels der Komponente b), bezogen auf die Präparation,
0,1 bis 200 Gew.-%, insbesondere 0,5 bis 100 Gew.-% eines Dispergiermittels der Komponente c), bezogen auf die Komponente a) gegebenenfalls bezogen auf die Summe der Komponenten a) und b) und
0 bis 98 Gew.-%, insbesondere 0,2 bis 98 Gew.-%, besonders bevorzugt 10 bis 98 Gew.-%, ganz besonders bevorzugt 30 bis 98 Gew.-% Wasser, bezogen auf die Pigmentpräparation.

Die Erfindung betrifft weiterhin ein Verfahren zur Herstellung der Pigmentpräparationen als Drucktinten für den Ink-Jet-Druck, das dadurch gekennzeichnet ist, daß man ein Pigment der Komponente a) und das Farbmittel b), insbesondere wenn es ein organisches oder anorganisches Pigment, oder ein wasserunlöslicher Farbstoff bzw. Weißtöner ist, mit mindestens einem Teil des Dispergiermittels c) und gegebenenfalls weiteren Zusätzen homogenisiert und gegebenenfalls naßzerkleinert.

Erfindungsgemäß umfaßt die Herstellung der Pigmentpräparationen gegebenenfalls eine Oberflächenmodifizierung von Pigmenten der Komp. a) in Wasser und/oder polarem organischem Lösungsmittel, um die aus der Pigmentherstellung erhaltenen "Rohpigmente" in die gewünschte Feinverteilung zu überführen und zu desagglomerieren bzw. zu desaggregieren. Verfahren hierzu sind beispielsweise in EP-0 650 945 A2 beschrieben.

Eine weitere Möglichkeit zur Desagglomerierung von Pigmenten der Komp. a) besteht in einer Vorbehandlung der Pigmentpulver mittels verdünnter Ammoniaklösung.

Erfindungsgemäß können Pigmentpräparationen enthaltend die Komp. a) sowie Pigmentpräparationen enthaltend Pigmente oder wasserunlösliche Farbmittel der Komp. b) alleine zunächst separat hergestellt werden und im Anschluß daran zu der erfindungsgemäßen Pigmentpräparation gemischt werden.

Im Falle der Verwendung wasserunlöslicher Farbmittel der Komponente b) wird im allgemeinen das Pigment der Komponenten a), gegebenenfalls nach Oberflächenmodifizierung, gegebenenfalls zusammen mit den mitzuverwendenden Farbmitteln der Komponente b) in Pulverform oder in Form- der wasserfeuchten Preßkuchen zusammen mit wenigstens einem Teil des Dispergiermittels und Wasser, vorzugsweise deionisiertem Wasser, zu einer homogenen Mahlsuspension beispielsweise mittels Rührwerksbütte, Dissolver und ähnlichen Aggregaten gegebenenfalls nach einer Vorzerkleinerung angeschlagen (d. h. eingebracht und homogenisiert).

Die Mahlsuspension kann außerdem Anteile niedrigsiedender Lösungsmittel (Siedepunkt < 150°C) enthalten, die im Verlauf der anschließenden Feinmahlung durch Verdampfung ausgetragen werden können. Sie kann aber auch Anteile höhersiedender Lösungsmittel oder weiterer Zusätze, wie sie oben beschrieben sind z. B. Mahlhilfs-, Entschäumungs- oder Benetzungsmittel, enthalten.

Die Naßzerkleinerung der Komp. a) oder der Komp. b), oder gemeinsam a) + b) umfaßt sowohl die Vorzerkleinerung als auch die Feinmahlung. Vorzugsweise liegt die Pigmentkonzentration der Suspension dabei oberhalb der gewünschten Konzentration der fertigen Pigmentpräparation bzw. Drucktinte. Die gewünschte Pigmentendkonzentration wird vorzugsweise im Anschluß an die Naßzerkleinerung eingestellt. Im Anschluß an die Vorzerkleinerung erfolgt eine Mahlung auf die gewünschte Partikelfeinverteilung. Für diese Mahlung kommen Aggregate wie z. B. Kneter, Walzenstühle, Knetschnecken, Kugelmühlen, Rotor-Stator-Mühlen, Dissolver, Korundscheibenmühlen, Schwingmühlen und insbesondere schnellaufende, kontinuierlich oder diskontinuierlich beschickte Rührwerkskugelmühlen mit Mahlkörpern mit einem Durchmesser von 0, 1 bis 5 mm in Frage. Die Mahlkörper können dabei aus Glas, Keramik oder Metall, z. B. Stahl sein. Die Mahltemperatur liegt vorzugsweise im Bereich von 0 bis 250°C, in der Regel jedoch bei Raumtemperatur, insbesondere unterhalb des Trübungspunktes des eingesetzten Dispergiermittels der Komponente c) und des gegebenenfalls eingesetzten grenzflächenaktiven Mittels.

In einer ebenfalls bevorzugten Verfahrensweise kann die Mahlung teilweise oder vollständig in einem Hochdruckhomogenisator oder in einem sogenannten Strahldispergator (bekannt aus DE-A 195 36 845) erfolgen, wodurch der Gehalt an Mahlkörperabrieb in der Suspension bzw. die Abgabe von löslichen Stoffen aus den Mahlkörpern (z. B. Ionen aus Glaskörpern) auf ein Minimum reduziert bzw. vollständig vermieden werden kann.

In einem Verdünnungs-Schritt wird die erhaltene Pigmentpräparation in an sich bekannter Weise in Wasser gegebenenfalls mit den restlichen Dispergiermittelmengen und gegebenenfalls weiteren Zusätzen eingemischt und homogenisiert, sowie auf die gewünschte Pigmentendkonzentration bzw. Farbstärke der Präparation bzw. Drucktinte eingestellt. Hierbei kann gegebenenfalls noch ein Teil des Dispergiermittels zugesetzt werden, um beispielsweise eine Reagglomeration feiner Pigmentpartikel in der Verdünnung zu vermeiden.

Von besonderem Vorteil ist ein Verfahren zur Herstellung der Pigmentpräparationen, in dem im Mahlschritt zur Herstellung des Pigmentkonzentrates für die Stabilisierung ausreichend Dispergiermittel zur Verfügung gestellt wird. Im

6. Pigmentpräparationen gemäß Anspruch 1, dadurch gekennzeichnet, daß als Farbmittel der Komponente b) organische und anorganische Pigmente, Ruß oder wasserlösliche und wasserunlösliche Farbstoffe oder optische Aufheller eingesetzt werden.

7. Pigmentpräparationen gemäß Anspruch 1, dadurch gekennzeichnet, daß sie zusätzlich ein organisches Lösungsmittel aus der nachstehenden Gruppe enthalten: aliphatische C_1-C_4-Alkohole, wie Methanol, Ethanol, Isopropanol, n-Propanol, n-Butanol, Isobutanol oder tert.-Butanol, aliphatische Ketone, wie Aceton, Methylethylketon, Methylisobutylketon oder Diacetonalkohol, Polyole, wie Ethylenglykol, Propylenglykol, Butylenglykol, Diethylenglykol, Triethylenglykol, Trimethylolpropan, Polyethylenglykol mit einem mittleren Molgewicht von 100 bis 4000, vorzugsweise 400 bis 1500 g/mol oder Glycerin, Monohydroxyether, vorzugsweise Monohydroxyalkylether, besonders bevorzugt Mono-C-C_4-alkylglykolether wie Ethylenglykolmonoalkyl-, -monomethyl-, -diethylenglykolmonomethylether oder Diethylenglykolmonoethylether, Diethylenglykolmonobutylether, Dipropylenglykolmonoethylether, Thiodiglykol, Triethylenglykolmonomethylether oder -monoethylether, ferner 2-Pyrrolidon, N-Methyl-2-pyrrolidon, N-Ethyl-pyrrolidon, N-Vinyl-pyrrolidon, 1,3-Dimethyl-imidazolidon, Dimethylacetamid sowie Dimethylformamid oder Mischungen davon.

8. Pigmentpräparationen gemäß Anspruch 1, enthaltend:
0,01 bis 20 Gew.-%, vorzugsweise 0,1 bis 10 Gew.-%, der Komponente a), bezogen auf die Komponente b),
1 bis 99,95 Gew.-%, vorzugsweise 1 bis 65 Gew.-% eines Farbmittels der Komponente b), bezogen auf die Präparation,
0 bis 200 Gew.-%, insbesondere 0 bis 100 Gew.-% eines Dispergiermittels der Komponente c), bezogen auf die Komponente a), gegebenenfalls auf die Summe der Komponenten a) und b) und
0 bis 98 Gew.-%, insbesondere 0,2 bis 98 Gew.-% Wasser, bezogen auf die Pigmentpräparation.

9. Verwendung der Pigmentpräparationen gemäß Anspruch 1 als Drucktinten für den Ink-Jet-Druck.

10. Verwendung der Pigmentpräparationen gemäß Anspruch 1, zum Pigmentieren natürlicher oder synthetischer Materialien, insbesondere von Dispersionsanstrichfarben, Druckfarben, wasserverdünnbaren Lacksystemen und Automobillacken sowie zum Pigmentieren von Kunststoffen und Papier in der Masse und als Papierstrichfarbe.

11. Verwendung der Pigmentpräparationen gemäß Anspruch 1 zur Herstellung von Drucktinten für den Ink-Jet-Druck.

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(54) PREPARATIONS PIGMENTEES CONTENANT DES PIGMENTS INORGANIQUES.
(54) INORGANIC PIGMENTS CONTAINING PIGMENT PREPARATIONS

(57)

The invention relates to pigment preparations containing a) solid compounds from the groups of oxides of titanium, zinc, tin, tungsten, molybdenum, nickel, bismuth, cerium, indium, hafnium, iron and/or silicon carbide, zinc sulfide, barium titanate, calcium titanate and/or silicon and/or solid silicon compounds in which silicon is available in stoichiometric surplus, with primary particles having a mean diameter of 500 nm, and b) at least one coloring agent which distinguishes itself from the solid compounds named under a). The inventive pigment preparations are characterized by a good resistance to light of the substrates colored with said preparations.

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(54) **PREPARATIONS PIGMENTEES CONTENANT DES PIGMENTS INORGANIQUES.**

(54) **INORGANIC PIGMENTS CONTAINING PIGMENT PREPARATIONS**

(57) L'invention concerne des préparations pigmentées contenant a) des composés solides du groupe des oxydes de titane, de zinc, d'étain, de wolfram, de molybdène, de nickel, de bismuth, de cérium, d'indium, d'hafnium, de fer et/ou de carbure de silicium, de sulfure de zinc, de titanate de baryum, de titanate de calcium et/ou de silicium et/ou de composés solides de silicium, dans lesquels le silicium est en excédent stoechiométrique, le diamètre moyen des particules primaires étant < 500 nm, et b) au moins un colorant distinct des composés solides cités en a). Ces préparations pigmentées sont caractérisées par la bonne résistance à la lumière des supports colorés avec ces préparations.

(57) The invention relates to pigment preparations containing a) solid compounds from the groups of oxides of titanium, zinc, tin, tungsten, molybdenum, nickel, bismuth, cerium, indium, hafnium, iron and/or silicon carbide, zinc sulfide, barium titanate, calcium titanate and/or silicon and/or solid silicon compounds in which silicon is available in stoichiometric surplus, with primary particles having a mean diameter of <500 nm, and b) at least one coloring agent which distinguishes itself from the solid compounds named under a). The inventive pigment preparations are characterized by a good resistance to light of the substrates colored with said preparations.

(57) Abstract

The invention relates to pigment preparations containing a) solid compounds from the groups of oxides of titanium, zinc, tin, tungsten, molybdenum, nickel, bismuth, cerium, indium, hafnium, iron and/or silicon carbide, zinc sulfide, barium titanate, calcium titanate and/or silicon and/or solid silicon compounds in which silicon is available in stoichiometric surplus, with primary particles having a mean diameter of $\leq$500 nm, and b) at least one coloring agent which distinguishes itself from the solid compounds named under a). The inventive pigment preparations are characterized by a good resistance to light of the substrates colored with said preparations.

Pigment preparations comprising inorganic pigments

The invention relates to pigment preparations comprising inorganic pigments, especially silicon or silicon compounds, to processes for preparing them and to their use, especially as printing inks for ink-jet printing.

Aqueous preparations of colorants, as are used, for example, for ink-jet printing, comprise as colorants not only water-soluble dyes but also organic and inorganic colour pigments and carbon blacks. Organic dyes, for example, when used in ink-jet printing generally give strongly coloured prints of high brilliance, but as compared with colour pigments possess poorer light fastness. In comparison to inorganic pigments, organic pigments often possess the disadvantage of inadequate light fastness and are therefore often unsuitable for use in a variety of applications. e.g. in the exterior sector.

With other applications of liquid colorant preparations as well, improving the light fastness, in particular, is continually part of numerous efforts.

The object of the present invention is therefore to provide coloured pigment preparations which in particular in ink-jet printing exhibit improved light fastness in combination with high optical density and brilliance.

Pigment preparations have now been found comprising

a) solid compounds from the group consisting of the oxides of titanium, zinc, tin, tungsten, molybdenum, nickel, bismuth, cerium, indium, hafnium, iron and/or silicon carbide, zinc sulphide, barium titanate, calcium titanate and/or silicon and/or solid silicon compounds in which silicon is present in stoichiometric excess, having an average diameter of the primary particles of <500 nm, preferably <150 nm, in particular <120 nm,

b) at least one colorant other than the solid compounds specified under a),

c) optionally a dispersant and

d) optionally water.

The presence of the two components c) and d) is preferred.

Silicon and the silicon compounds of component a) have already been disclosed in the as yet unpublished DE-A-19 647 294.

Elemental silicon comprises amorphous or crystalline silicon, preferably crystalline silicon. The size of the silicon particles is preferably between 1 nm and 120 nm, with particular preference between 1 nm and 70 nm, with very particular preference between 5 nm and 50 nm. These particles preferably have a size distribution with a half-value width of 40 nm or less. Silicon particles having this mean diameter are preferably prepared by gas-phase reaction (CVR) in accordance with the process described in US-A 5 472 477. Likewise possible is preparation in accordance with the further processes specified in DE-A 19 647 294.

The term solid compounds covers compounds which are solid at room temperature, examples being silicides, $CaSi_2$ and/or $BaSi_2$. The term "compounds in which silicon is present in stoichiometric excess" preferably covers compounds of the formula Si_XZ_{1-X} where $x > 0.5$, preferably $x > 0.7$ and Z = C, N, O, Ge, Ca, Ba and Sr. The presence of other materials shifts the energetic position of the absorption edge within certain limits and modifies the shape of the edge. Preferred solid compounds here are Si_XC_{1-X} or Si_XGe_{1-X}.

In one preferred embodiment of the invention, the solid compounds in which silicon is present in stoichiometric excess have a core/shell structure. The average diameter

of the primary particles is preferably less than 120 nm, with particular preference less than 100 nm, with very particular preference less than 50 nm. These particles preferably have a size distribution with a half-value width of 40 nm or less. The particle preferably consists of a titanium nitride core and a silicon shell, the volume fraction of the silicon preferably being at least 30% per particle.

In another preferred embodiment of the invention, the silicon component a) comprises shell particles in the form of a solid compound consisting of silicon and materials which are more strongly absorbing in the red spectral range (600 nm $< \lambda <$ 700 nm) than those in the blue-green (400 nm $< \lambda <$ 550 nm) spectral range.

The preparation of the silicon component a) is likewise disclosed in DE-A-19 647 294 (p. 5, para. 1 of the priority text) and is subject-matter of this specification.

In one preferred embodiment, the primary particles of the silicon component a) are spherical. They may also be present in the form of aggregates or agglomerates.

The primary particles of the silicon component a) may also be surrounded by an oxide layer which prevents direct aggregation of the Si primary particles, thereby preventing their agglomeration. The thickness of the oxide layer is preferably from 1 nm to 300 nm, with particular preference from 10 to 100 nm. This oxide layer can be effected, for example, by metering oxygen into the CVR reactor following the preparation of the particles. The oxide layer preferably consists of SiO_2.

The preparations of the invention preferably contain from 0.01 to 500, in particular from 0.01 to 250% by weight, in particular from 0.01 to 20% by weight of component a), based on the colorant of component b).

Examples of suitable colorants of component b) are organic pigments and inorganic pigments other than those of component a), and also carbon black or water-soluble and water-insoluble dyes, the term dyes also embracing optical brighteners.

Suitable carbon blacks are, in particular, acidic to alkaline blacks from the group of the furnace or gas blacks, and also chemically or physically modified or aftertreated carbon blacks; examples of suitable inorganic pigments are zinc sulphides, ultramarine, iron oxides, cobalt blue and also chromium oxide pigments and also pigments in the form of finely particulate oxides such as silicon dioxide, titanium dioxide, nickel oxides, chromium antimony titanium dioxides, aluminium oxide, and also finely particulate metals such as copper, iron or aluminium; and examples of suitable organic colour pigments are those of the azo, disazo, polyazo, anthraquinone and thioindigo series, and also other polycyclic pigments such as, for example, those from the phthalocyanine, quinacridone, dioxazine, isoindolinone, naphthalenetetracarboxylic acid and perylene and perylenetetracarboxylic acid series, and also those from the perinone, indigoid, thioindigoid and diketopyrrolopyrrole series, and also metal complex pigments of azo, azomethine or methine dyes, or laked dyes such as Ca, Mg, Al lakes of dyes containing sulphonic acid and/or carboxylic acid groups.

Examples of water-soluble organic dyes are acidic and basic dyes, and examples of water-insoluble dyes are disperse dyes or whiteners (optical brighteners). Examples of disperse dyes that may be mentioned are those from the azo, disazo, anthraquinone, coumarin, isoindolenine, quinoline and methine series.

In one preferred embodiment, the preparation of the invention comprises as colorant oxides and/or nitrides of metals which absorb more strongly in the red spectral range of $600\ nm < \lambda < 700\ nm$ than in the blue-green spectral range of $400\ nm < \lambda < 550\ nm$. This is particularly the case when using pigments having an intrinsic yellow to orange coloration. Preferred such additives are pigments comprising titanium nitride having an average diameter of from 1 nm to 400 nm, preferably from 10 nm to 120 nm, or its agglomerates. They can be prepared, for

example, in accordance with US-A 5 472 477. Likewise preferred colorants are ultramarine pigments, obtainable for example from the company Nubiola S.A., under the designation Nubix® pigments. Preference is given, furthermore, to iron(III) hexacyanoferrate(II). Preference is also given to pigments of iridium oxide doped with more than 5% by weight with tin.

The particle size of the other representatives of component a) is preferably from 1 nm to 500 nm, with particular preference from 1 nm to 120 nm. These as well are obtainable, inter alia, in accordance with the process described in US-A 5 472 477.

Dispersants

Dispersants are preferably regarded as being molecules having a molar mass of from 1000 to 500,000, preferably from 1000 to 100,000 and, in particular, from 1000 to 10,000 g/mol. The dispersants can be nonionic, anionic, cationic or amphoteric compounds.

Examples of nonionic dispersants are the following: alkoxylates, alkylolamides, esters, amine oxides and alkyl polyglycosides.

Further suitable nonionic dispersants are the following: reaction products of alkylene oxides with alkylatable compounds, such as fatty alcohols, fatty amines, fatty acids, phenols, alkylphenols, arylalkylphenols, such as styrene-phenol condensates, carboxamides and resin acids, for example. These dispersants are, for example, ethylene oxide adducts from the class of the reaction products of ethylene oxide with:

a) saturated and/or unsaturated fatty alcohols having 6 to 20 carbon atoms or

b) alkylphenols having 4 to 12 carbon atoms in the alkyl radical or

c) saturated and/or unsaturated fatty amines having 14 to 20 carbon atoms or

d) saturated and/or unsaturated fatty acids having 14 to 20 carbon atoms or

e) hydrogenated and/or unhydrogenated resin acids.

Particularly suitable ethylene oxide adducts are the alkylatable compounds specified under a) to e) with from 5 to 120, preferably from 5 to 60, in particular from 5 to 30, mol of ethylene oxide.

Particular preference is given to nonionic polymeric dispersants.

Examples of dispersants regarded as polymeric are the compounds listed in the index "Water-Soluble Synthetic Polymers: Properties and Behavior" (Volumes I + II by Philip Molyneux, CRC Press, Florida 1983/84).

Examples of further suitable polymeric dispersants are water-soluble and water-emulsifiable compounds, e.g. homopolymers and copolymers, graft polymers and graft copolymers, and also random block copolymers.

Examples of particularly preferred polymeric dispersants are AB, BAB and ABC block copolymers. In the AB or BAB block copolymers, the A segment is a hydrophobic homopolmyer or copolymer which ensures a connection to the pigment and the B block is a hydrophilic homopolymer or copolymer or a salt thereof and ensures the dispersing of the pigment in the aqueous medium. Polymeric dispersants of this kind and their synthesis are known, for example, from EP-A-518 225 and EP-A-556 649.

Further examples of suitable polymeric dispersants are polyethylene oxides, polypropylene oxides, polyoxymethylenes, polytrimethylene oxides, polyvinyl methyl ethers, polyethyleneimines, polyacrylic acids, polyarylamides, polymethacrylic acids,

polymethacrylamides, poly-N,N-dimethyl-acrylamides, poly-N-isopropylacrylamides, poly-N-acryloylglycinamides, poly-N-methacryloylglycinamides, polyvinyl alcohols, polyvinyl acetates, copolymers of polyvinyl alcohols and polyvinyl acetates, polyvinylpyrrolidone, polyvinyloxazolidones, polyvinylmethyloxazolidones.

Also of importance are natural polymeric dispersants such as cellulose, starch, gelatin or derivatives thereof as polymeric dispersants. Particularly suitable polymers are those comprising amino acid units, e.g. polylysine, polyaspartic acid etc.

Examples of anionic dispersants are the following: alkyl sulphates, ether sulphates, ether carboxylates, phosphate esters, sulphosucinates, sulphosuccinate amides, paraffinsulphonates, olefinsulphonates, sarcosinates, isothionates, taurates, and lignin-type compounds.

Particular preference is given to anionic polymeric dispersants.

Suitable anionic polymeric dispersants are, in particular, condensation products of aromatic sulphonic acids with formaldehyde, such as condensation products of formaldehyde and alkylnaphthalenesulphonic acids or of formaldehyde, naphthalenesulphonic acids and/or benzenesulphonic acids, and condensation products of optionally substituted phenol with formaldehyde and sodium bisulphite.

Also suitable are condensation products obtainable by reacting naphthols with alkanols, subjecting the product to addition reaction with alkylene oxide, and converting at least some of the terminal hydroxyl groups into sulpho groups or monoesters of maleic acid, phthalic acid or succinic acid.

Also suitable, moreover, are dispersants from the group of the sulphosuccinic esters, and also alkylbenzenesulphonates. Moreover, sulphated, alkoxylated fatty acid alcohols or salts thereof. Alkoxylated fatty acid alcohols are in particular saturated or unsaturated C_6-C_{22} fatty acid alcohols, especially stearyl alcohol, which have been

provided with from 5 to 120, preferably from 5 to 60, in particular from 5 to 30 ethylene oxide. Particular preference is given to stearyl alcohol alkoxylated with from 8 to 10 ethylene oxide units. The sulphated alkoxylated fatty acid alcohols are preferably in salt form, especially as alkali metal or amine salts, preferably as the diethylamine salt.

Further examples of anionic polymeric dispersants are the salts of polyacrylic acids, polyethylenesulphonic acids, polystyrenesulphonic acid, polymethacrylic acids and polyphosphoric acids.

Additional examples of anionic polymeric dispersants are copolymers of acrylic monomers, which are indicated by way of example in the following table by a combination of the following monomers, which are synthesized to random, alternating or graft copolymers:

acrylamide,	acrylic acid;
acrylamide,	acrylonitrile;
acrylic acid,	N-acryloylglycinamide;
acrylic acid,	ethyl acrylate;
acrylic acid,	methyl acrylate;
acrylic acid,	methylenebutyrolactam;
N-acryloylglycinamide,	N-isopropylacrylamide;
methacrylamide,	methacrylic acid;
methacrylic acid,	benzyl methacrylate;
methacrylic acid,	diphenylmethyl methacrylate;
methacrylic acid,	methyl methacrylate;
methacrylic acid,	styrene.

Further anionic polymeric dispersants are styrene-maleic anhydride copolymers, copolymers thereof with the abovementioned acrylic monomers, and also

polyurethane-based polymers, e.g. those based on star-branched oligourethanes as per EP-A 331 066 or EP-A 400 410.

Also suitable are graft polymers and graft copolymers where nonionic and/or anionic vinyl monomers have been grafted onto a polymeric base. Synthetic or natural protective colloids can be used as the polymeric base.

Also particularly suitable are ligninsulphonates, e.g. those obtained by the sulphite or kraft process. They are preferably products which in part are hydrolysed, oxidized, propoxylated, sulphonated, sulphomethylated or disulphonated and fractionated by known processes, for example in accordance with the molecular weight or in accordance with the degree of sulphonation. Mixtures of sulphite and kraft ligninsulphonates are also highly effective. Particularly suitable ligninsulphonates are those having an average molecular weight of more than 1000 to 100,000, an active ligninsulphonate content of at least 80% and, preferably, a low polyvalent cation content. The degree of sulphonation can vary within wide limits.

Examples of cationic dispersants are as follows: quaternary alkylammonium compounds and imidazoles.

Particular preference is given to cationic polymeric dispersants.

Examples of cationic polymeric dispersants are the salts of polyethyleneimines, polyvinylamines, poly(2-vinylpyridines), poly(4-vinylpyridines), poly(diallyl-dimethylammonium) chloride, poly(4-vinylbenzyltrimethylammonium) salts and poly(2-vinylpiperidine).

Examples of amphoteric dispersants are the following compounds: betaines, glycinates, propionates and imidazolines.

Anionic and cationic polymers are summarized as polyelectrolytes and are fully or partly dissociable in an aqueous and/or organic phase.

The dispersant used is used preferably in an amount of from 0.1 to 200% by weight, in particular from 0.5 to 100% by weight, based on components a) and optionally b).

If water-insoluble dyes or pigments or carbon black are used as colorants, then the amount of dispersant used is based preferably on the sum of components a) and b).

In addition to the dispersant used, the pigment preparations of the invention may also comprise further cationic, anionic, amphoteric and/or nonionic and/or surface-active compounds, examples being those listed in the index "Surfactants Europa, A. Directory of surface Active Agents available in Europe" (Edited by Gordon L. Hollis, Royal Socity of Chemistry, Cambridge (1995).

Where the dispersant used contains ionic groups, these auxiliaries should preferably be nonionic or of the same ionicity.

Especially the pigment preparations which are used as printing inks for ink-jet printing preferably contain as further component e) an organic solvent.

Suitable organic solvents (e) are: aliphatic C_1-C_4-alcohols, such as methanol, ethanol, isopropanol, n-propanol, n-butanol, isobutanol or tert-butanol, 1,5-pentadiol, aliphatic ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or diacetone alcohol, polyols, such as ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, triethylene glycol, trimethylolpropane, polyethylene glycol having an average molar weight of from 100 to 4000, preferably from 400 to 1500 g/mol or glycerol, monohydroxy ethers, preferably monohydroxyalkyl ethers, with particular preference mono-C_1-C_4-alkyl glycol ethers such as ethylene glycol monoalkyl, monomethyl, diethylene glycol monomethyl ether or diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, dipropylene glycol monoethyl ether,

thiodiglycol, triethylene glycol monomethyl ether or monoethyl ether, and also 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethylpyrrolidone, N-vinyl-pyrrolidone, 1,3-dimethyl-imidazolidone, dimethylacetamide and dimethylformamide.

Also suitable are mixtures of the abovementioned solvents.

The amount of organic solvent is preferably from 0 to 40, in particular from 2 to 20% by weight, based on the pigment preparations.

Preferably, the amount of water and organic solvent is from 20 to 99% by weight, preferably from 30 to 97% by weight, based on the pigment preparations.

The pigment preparations may further comprise agents for adjusting the viscosity of the ink, such as, for example, polyvinyl alcohol, polyvinylpyrrolidone, methylcellulose and other agents known to the person skilled in the art, provided that they do not adversely affect the stability of the printing ink, the printing behaviour and the drying behaviour on paper.

As a further addition, compounds from the group of the terpenes, terpenoids, fatty acids and fatty acid esters are to be mentioned. Preferred compounds that may be mentioned include:

ocimene, myrcene, geraniol, nerol, linalool, citronellol, geranial, citronellal, neral, limonene, menthol, for example (-)-menthol, menthol or bicyclic monoterpenes, saturated and unsaturated fatty acids having 6 to 22 carbon atoms, such as for example stearic acid, oleic acid, linoleic acid and linolenic acid or mixtures thereof.

In principle the pigment preparations may include further additives such as preservatives (biocides), further wetting agents or surfactants, spacers, flatting agents, stabilizers, further UV absorbers, plasticizers, lubricants and optionally pH regulators.

Examples of suitable biocides are isothiazolones and benzisothiazolones.

Suitable spacers or flatting agents have average particle diameters in particular in the range from 0.2 µm to 30 µm and are described, for example, in DE 3 331 542. The spacers are preferably water-insoluble and resistant to the solvent additions used in the inks. Examples of suitable spacers or flatting agents are polymethyl methacrylate, polystyrene, styrene-divinylbenzene copolymer, crosslinked polymethyl methacrylate, and crosslinked or non-crosslinked polyvinyltoluene.

Suitable stabilizers are o-, m- and p-dihydroxybenzenes, hydroxychromans, 5-hydroxycumarans, spirochromans, spiroindanes, p-alkoxyphenols, sterically hindered phenols, gallic acid derivatives, methylenedioxybenzenes, aminophenols, aminoanilines, sterically hindered amines, derivatives having esterified or etherified phenolic hydroxyl groups, and derivatives having acylated or alkylated aromatic amino groups, metal complexes.

Particularly suitable stabilizers are sterically hindered amines, preferably compounds based on 2,2,6,6-tetraalkylpiperidine, with particular preference compounds based on 2,2,6,6-tetraalkylpiperidine which contain at least one covalently bonded 2,2,6,6-tetraalkylpiperidine fragment.

In many cases, the use of certain combinations of colour image stabilizers has proven to be particularly effective.

Suitable UV absorbers are described, for example, in DE 195 03 885.

Plasticizers and lubricants used are, for example, core-shell latices having a soft core and a hard shell, latices which consist of a soft core and a shell of crosslinked gelatine, and those with soft intermediate layers.

Examples of pH regulators are NaOH, ammonia or aminomethylpropanol, N,N-dimethylaminoethanol.

Examples of preservatives are methyl- and chloromethylisothiazolin-3-one, benzisothiazolin-3-one or mixtures thereof.

As a further particular embodiment of the invention, there are the pigment preparations of the invention comprising in addition to components a) and b) and optionally c) and d), in addition, sterically hindered amines, preferably those based on 2,2,6,6-tetraalkylpiperidine, with particular preference compounds based on 2,2,6,6-tetraalkylpiperidine which contain at least one covalently bonded 2,2,6,6-tetraalkylpiperidine fragment.

The pigment preparations of the invention contain preferably:

from 0.01 to 500% by weight, preferably from 0.01 to 250% by weight, in particular from 0.01 to 20% by weight of component a), based on the colorant of component b).

from 1 to 99.95% by weight, preferably from 1 to 65% by weight of a colorant of component b), based on the preparation,

from 0.1 to 200% by weight, in particular from 0.5 to 100% by weight of a dispersant of component c), based on the component a) optionally based on the sum of components a) and b), and

from 0 to 98% by weight, in particular from 0.2 to 98% by weight, with particular preference from 10 to 98% by weight, with very particular preference from 30 to 98% by weight of water, based on the pigment preparation.

The invention further relates to a process for preparing the pigment preparations as printing inks for ink-jet printing, which is characterized in that a pigment of

component a) and the colorant b), especially if it is an organic or inorganic pigment, or is a water-insoluble dye or whitener, is homogenized with at least part of the dispersant c) and optionally further additives and this homogenized mixture is optionally subjected to wet comminution.

In accordance with the invention, preparing the pigment preparations includes optionally a surface modification of pigments of comp. a) in water and/or polar organic solvent, in order to convert the "crude pigments" obtained from the pigment production into the desired state of fine division and in order to deagglomerate and/or deaggregate them. Processes for this purpose are described, for example, in EP-0 650 945 A2.

A further possibility for deagglomerating pigments of comp. a) is to pretreat the pigment powders by means of dilute ammonia solution.

In accordance with the invention, pigment preparations comprising comp. a) and also pigment preparations comprising pigments or water-insoluble colorants of comp. b) alone can be prepared separately first of all and subsequently can be mixed to give the pigment preparation of the invention.

In the case of the use of water-insoluble colorants of component b), the pigment of component a), optionally after surface modification, optionally together with the colorants of component b) in powder form or in the form of the water-moist presscakes, together with at least some of the dispersant and water, preferably deionized water, is generally beaten (i.e. introduced and homogenized) to a homogenous milled suspension by means, for example, of a stirring vat, dissolver and similar equipment, optionally after a precomminution stage.

The milled suspension may further contain fractions of low-boiling solvents (boiling point < 150°C) which may be carried off by evaporation in the course of the subsequent fine grinding. However, it may also include fractions of higher-boiling

solvents or further additives, as are described above, e.g. grinding aids, defoamers or wetting agents.

The wet comminution of comp. a) or of comp. b), or a) + b) together, embraces both the precomminution and the fine grinding. In this case, the pigment concentration of the suspension is preferably above the desired concentration of the finished pigment preparation or printing ink. The desired final pigment concentration is preferably established following wet comminution. Following precomminution, grinding takes place to the desired state of particle fine division. Suitable milling equipment for this grinding stage comprises, for example, kneading apparatus, roll mills, kneading screws, ball mills, rotor-stator mills, dissolvers, corundum disc mills, vibratory mills and especially high-speed, continuously or discontinuously charged stirred ball mills containing grinding media having a diameter of from 0.1 to 5 mm. The grinding media can be of glass, ceramic or metals, e.g. steel. The grinding temperature is preferably within a range from 0 to 250°C, but generally lies at room temperature, in particular below the cloud point of the dispersant of component c) that is used and of the optionally used surface-active agent.

In a likewise preferred procedure, grinding can take place in part or in whole in a high-pressure homogenizer or in a so-called jet disperser (known from DE-A 19 536 845), by means of which the amount of grinding media detritus in the suspension, and/or the release of soluble substances from the grinding media (i.e. ions from glass media), can be reduced to a minimum or avoided completely.

In a dilution step, the resulting pigment preparation is mixed in a manner known per se into water, optionally with the remaining amounts of dispersant and optionally further additives, and homogenized, and is adjusted to the desired final pigment concentration or colour strength of the preparation or printing ink. In this case, it is optionally possible to add a further part of the dispersant in order, for example, to prevent reagglomeration of fine pigment particles in the dilution.

Of particular advantage is a process for preparing the pigment preparations in which in the grinding step for preparing the pigment concentrate sufficient dispersant is made available for stabilization. Subsequently thereto or after dilution with water, excess surface-active agents and/or dispersant that is present in solution and is not adsorbed on the pigment is preferably removed and, subsequently, the desired pigment preparation is standardized by adding the remaining fractions of the pigment preparation.

A method of removing dispersant present in solution is, for example, the centrifugation of the suspension and subsequent decantation of the supernatant. Membrane filtration or microfiltration techniques are also suitable.

Furthermore, it is possible to add other additives, such as, for example, polyurethane polymers or acrylic polymers in order, optionally, to improve further the water fastness. These polymers may be either water-soluble or else water-emulsifiable in nature, or may be soluble in one of the components present in b).

In a preferred procedure, the pigment preparations are mixed and homogenized using a jet disperser or high-pressure homogenizer in order to suppress the formation of foam and to prevent possible reagglomeration.

The standardization of the desired pigment preparations is accompanied by standardization to the desired viscosity, colour strength, hue, density and surface tension of the ink.

Before the use of the pigment preparations as printing inks, the inks are optionally fine-filtered by means, for example, of 0.5 to 5 μm membrane filters or glass filters.

In general, the physical ink properties are standardized to use in conventional ink-jet printers, the surface tension being preferably between 20 and 70 mN/m and the viscosity being preferably less than 20 mPa s, in particular from 0.5 to 10 mPa s.

The printing inks of the invention and the printing inks used in accordance with the invention, when used as printing ink in ink-jet printing, give prints having excellent light fastness and high optical density, and further possess the following advantages: outstanding dispersion stability and storage stability within a wide temperature range, no blockage in the printing head (known as cogation or clogging), high water fastness and migration fastness of the prints on various substrates, e.g. on mechanical paper, medium-grade paper, sized and coated paper, polymeric films, transparencies for overhead projection, no bleeding in multi-colour printing, even when used together with dye inks or other pigmented inks.

The pigment preparations described above are used preferably as printing inks for ink-jet printing.

Ink-jet printing is known per se and generally takes place such that the printing ink is filled into an acceptor vessel of an ink-jet printing head and is sprayed in small droplets onto the substrate. The ejection of the ink in droplet form takes place preferably by way of a piezoelectric crystal, a heated cannula (bubble-jet or thermo-jet process) or by mechanical pressure increase, where pressure is exerted on the ink system and drops of ink are ejected accordingly. The droplets are fired from one or more small nozzles in a targeted manner onto the substrate such as, for example, paper, wood, textiles, plastic or metal. Under electronic control, the individual droplets are collated on the substrate to form textual symbols or graphic patterns.

Also possible is a process in which, by means of electrostatic deflection, very small volumes in the form of drops are brought onto a substrate from one jet of ink.

The invention further relates to the use of the pigment preparations as printing inks for ink-jet printing and for pigmenting and colouring natural or synthetic materials, especially plastics, leather and paper in the mass and on the surface.

In particular, the pigment preparations are also suitable for preparing automotive paints, emulsion paints, dispersion coating materials, printing inks, water-dilutable coating systems, aqueous flexographic and gravure inks, wallpaper colours, aqueous wood preservative systems and woodstains, renders, and for pigmenting coloured pencil leads, fibre-tip pens, ink-jet inks, Indian inks, pastes for ballpoint pens, chalks, laundry detergents and cleaning products, shoe polishes, non-woven webs, paper stock colourings, coloured paper coating slips, cardboard packaging printing inks, colouring of latex products, abrasives, spin dyeings and films.

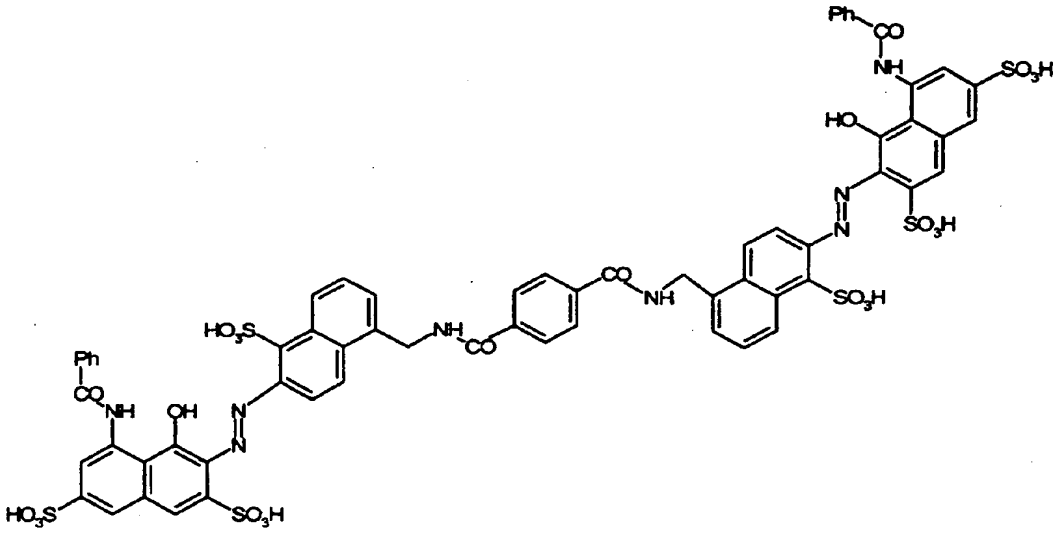
With particular preference, the pigment preparations are used as printing inks for ink-jet printing.

Examples

Preparation and use of zinc oxide as light stabilizer in ink-jet inks

Example 1

A stock solution (A) (stock ink) of a magenta dye, in the form of the sodium salt, of the formula



having an E1/1 value of 12 was prepared by homogenous mixing of

22.8 g	of an aqueous, salt-free solution of the abovementioned magenta dye having an E1/1 value of 53, (pure dye content about 10.4% by weight)
6.2 g	of 1,5-pentadiol
6.2 g	of 2-pyrrolidone and
64.8 g	of water.

(E1/1 value: Extinction value of the longest-wavelength band in the light spectrum, obtained by measuring a 1% strength solution of the dye in a measuring cell with a path length of 1 cm.

Also prepared was a solvent mixture (B) consisting of

8.0 g of 1,5-pentanediol
8.0 g of 2-pyrrolidone
84.0 g of water.

Subsequently,

5 g of the stock solution (A)
4.4 g of the solvent mixture (B) and
0.6 g of an aqueous zinc oxide dispersion consisting of
30% by weight of zinc oxide having a primary particle diameter of 10 – 30 nm measured by means of transmission electron microscopy (TEM) or an agglomerate particle size determined, from which the following mass distribution resulted by means of measurement with an ultracentrifuge.
50% by mass of the particles smaller than 43 nm (d_{50} of 43 nm)
90% by mass of the particles smaller than 65 nm (d_{50} of 65 nm)
10% by mass of the particles smaller than 25 nm (d_{50} of 25 nm)
less than 2% by weight of polyacrylic acid and residual water
were homogeneously mixed to form a printing ink, and printing was carried out using a thermal ink-jet printer of the type HP Deskjet 500 C (from Hewlett Packard) by filling the

ink thus prepared into the black cartridge type HP 51626 A as a replacement for the ink originally present.
The ink of the invention was printable flawlessly and possesses very good storage stability.

Full-area prints were produced on standard paper (Agfa 701, Agfa-Gevaert) and on special ink-jet paper (HOMO-GENTISATE PHYTYLTRANSFERASE Premium, Hewlett-Packard) and the prints were subsequently exposed with xenon light whose intensity was 750 W/m^2 for 12 hours, UV light below a wavelength of 290 µm being excluded by means of a filter. The light fastness was evaluated on the basis of the residual colour difference DE* and of the hue angle difference Hab* in accordance with the Cielab system in comparison against the respective unexposed print.
The results are set out in Table 1.
The lower the value of the residual colour difference, the better the light fastness.

Example 2

As described in Example 1, a printing ink was prepared, consisting of

5 g of the stock solution (A),
2.5 g of the solvent mixture (B) and
2.5 g of the same zinc oxide dispersion as in Example 1, and was printed and tested as in Example 1.

Comparative example

As described in Example 1, a printing ink was prepared, consisting of

5 g of the stock solution (A) and
5 g of the solvent mixture (B)
without the addition of a light stabilizer and was printed and tested as in Example 1.

Table 1

		Cielab coord. unexposed print		after 12 h of exposure versus unexposed print	
Printing ink according to	Paper	C*	h*	DE*	H ab*
Example 1	AGFA 701	60.16	348.38	26.11	0.70
Example 2	AGFA 701	59.37	353.48	12.60	- 0.32
Comparative example	AGFA 701	62.92	349.94	35.42	2.50
Example 1	HP Premium	69.17	346.35	36.89	- 0.01
Example 2	HP Premium	64.87	355.41	8.24	- 1.73
Comparative example	HP Premium	69.52	349.30	59.13	3.25

It was found that the dye inks prepared and printed in accordance with Example 1 and 2 exhibit a markedly improved light fastness.

Patent Claims

1. Pigment preparations comprising

a) solid compounds from the group consisting of the oxides of titanium, zinc, tin, tungsten, molybdenum, nickel, bismuth, cerium, indium, hafnium, iron and/or silicon carbide, zinc sulphide, barium titanate, calcium titanate and/or silicon and/or solid silicon compounds in which silicon is present in stoichiometric excess, having an average diameter of the primary particles of <500 nm, and

b) at least one colorant other than the compounds specified under a).

2. Pigment preparations according to Claim 1, comprising

a) silicon and/or solid silicon compounds in which silicon is present in stoichiometric excess, having an average diameter of the primary particles of < 120 nm, and

b) at least one colorant.

3. Pigment preparations according to Claim 1, comprising as component a) solid compounds from the group consisting of the oxides of titanium, zinc, tin, tungsten, molybdenum, nickel, bismuth, cerium, indium, hafnium, iron and/or silicon carbide, zinc sulphide, barium titanate and/or calcium titanate having an average primary particle of < 120 nm.

4. Pigment preparations according to Claim 1, comprising in addition to components a) and b) at least one dispersant c) and water d).

5. Pigment preparations according to Claim 1, characterized in that the solid compounds in which silicon is present in stoichiometric excess are compounds of the formula Si_xZ_{1-x} where $x > 0.5$, preferably $x > 0.7$ and Z = C, N, O, Ge, Ca, Ba and Sr.

6. Pigment preparations according to Claim 1, characterized in that colorants of component b) used are organic and inorganic pigments, carbon black or water-soluble and water-insoluble dyes or optical brighteners.

7. Pigment preparations according to Claim 1, characterized in that they additionally comprise an organic solvent from the following group: aliphatic C_1-C_4-alcohols, such as methanol, ethanol, isopropanol, n-propanol, n-butanol, isobutanol or tert-butanol, 1,5-pentanediol, aliphatic ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or diacetone alcohol, polyols, such as ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, triethylene glycol, trimethylolpropane, polyethylene glycol having an average molar weight of from 100 to 4000, preferably from 400 to 1500 g/mol or glycerol, monohydroxy ethers, preferably monohydroxyalkyl ethers, with particular preference mono-C_1-C_4-alkyl glycol ethers such as ethylene glycol monoalkyl, monomethyl, diethylene glycol monomethyl ether or diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, dipropylene glycol monoethyl ether, thiodiglycol, triethylene glycol monomethyl ether or monoethyl ether, and also 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-pyrrolidone, N-vinyl-pyrrolidone, 1,3-dimethyl-imidazolidone, dimethyl-acetamide and dimethylformamide or mixtures thereof.

8. Pigment preparations according to Claim 1, comprising:

from 0.01 to 500% by weight, preferably from 0.01 to 250% by weight, in particular from 0.01 to 20% by weight of component a), based on component b),

from 1 to 99.95% by weight, preferably from 1 to 65% by weight of a colorant of component b), based on the preparation,

from 0 to 200% by weight, in particular from 0 to 100% by weight of a dispersant of component c), based on the component a), optionally on the sum of components a) and b), and

from 0 to 98% by weight, in particular from 0.2 to 98% by weight of water, based on the pigment preparation.

9. Pigment preparations according to Claim 1 additionally comprising a sterically hindered amine, preferably an amine based on 2,2,6,6-tetraalkylpiperidine, with particular preference one based on 2,2,6,6-tetraalkylpiperidine which contains at least one covalently bonded 2,2,6,6-tetraalkylpiperidine fragment.

10. Use of the pigment preparations according to Claim 1 as printing inks for ink-jet printing.

11. Use of the pigment preparations according to Claim 1, for pigmenting and colouring natural or synthetic materials, especially emulsion paints, printing inks, water-dilutable coating systems and automotive paints and also for pigmenting and colouring plastics, leather and paper in the mass and on the surface, especially coloured paper coating slip.

12. Use of the pigment preparations according to Claim 1 for preparing printing inks for ink-jet printing.

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